

STUDY IN COMETARY ASTROPHYSICS

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# ABSTRACT

Continuing investigations in cometary astrophysics have been directed toward the collisional processes occurring in comets. The reactions of NH and NH<sub>2</sub> in the decomposition of NH<sub>3</sub> have been examined. Shock tube studies of the vibrational relaxation of C<sub>2</sub> and the singlet-triplet collisional interchange in C<sub>2</sub> and NH have entailed the construction of specific flash lamps for future absorption measurements. The products from the electron bombardment of low-pressure gases have been identified as CO<sup>+</sup> emission.

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## 1. PHOTOCHEMISTRY: REACTIONS OF NH AND NH<sub>2</sub> RADICALS

### 1.1 Introduction

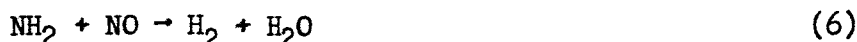
The presence of free radicals in the coma of comets raises the question of their origin in cometary atmospheres. The occurrence of collisions in a still-to-be defined region near the nucleus-coma interface requires that the reactions of these radicals with other radicals or with parent stable molecules be more fully understood. In an attempt to contribute to the ultimate solution of these problems, a re-examination of the relative importance of the formation of NH and NH<sub>2</sub> in the primary photochemical decomposition processes of NH<sub>3</sub> has been performed. Some reactions of NH and NH<sub>2</sub> are also discussed and their relative importance evaluated.

The generally accepted mechanism<sup>1</sup> for the photolysis of ammonia in the diffuse-banded region above 1600 Å is as follows:



The reaction of H with NH<sub>3</sub> is excluded because of its high activation energy ( $\sim 14$  kcal/mole)<sup>2</sup> as compared to  $\Delta E = 2$  kcal/mole<sup>3</sup> for reaction (2). The observation of high yields of N<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> and low yields of N<sub>2</sub> at short decomposition times and fast flow rates are consistent with this mechanism.<sup>4</sup> The mechanism requires that efficient scavenging of H atoms should inhibit not only H<sub>2</sub> formation via reactions (2) and (3) but also N<sub>2</sub> formation via reaction (4) since N<sub>2</sub>H<sub>3</sub> is only found in an H-atom abstraction reaction. Addition of

ethylene,<sup>5,6</sup> oxygen,<sup>7</sup> and nitric oxide<sup>8</sup> reduces the H<sub>2</sub> yield to less than 5% of its value in the absence of these molecules. In the presence of O<sub>2</sub> or NO, the N<sub>2</sub> production remains unchanged. However, this has been shown<sup>8</sup> to be due to the occurrence of



The production of N<sub>2</sub> in presence of C<sub>2</sub>D<sub>4</sub> has not been investigated.

At 1470 Å and 1236 Å, the additional primary process



has been suggested to occur to 12% and 14% respectively.<sup>5,6</sup> The reactions of NH<sub>2</sub> and NH radical in these systems have not been examined, but the occurrence of



or



could lead to the production of H<sub>2</sub> by reactions other than (2), (3), or (7). Since the relative importance of (7) was based on formation of H<sub>2</sub> in presence of C<sub>2</sub>D<sub>4</sub> which scavenges H atoms, occurrence of (8), (9), or similar reaction in the presence of C<sub>2</sub>D<sub>4</sub> could lead to an over-estimation of the importance of the direct production of molecular hydrogen and NH radicals.

Consequently, the production of both N<sub>2</sub> and H<sub>2</sub> in the photolysis of NH<sub>3</sub> in the presence of C<sub>2</sub>D<sub>4</sub> has been examined at wavelengths above and below 1600 Å.

## 1.2 Results and Discussion

1.2.1 Photolysis at 1849 Å: The production of hydrogen in the presence of 15% C<sub>2</sub>D<sub>4</sub> is reduced to an average of about 4% (table 1) of its value in the absence of C<sub>2</sub>D<sub>4</sub>. This may be compared with values



Table 1-1

Photolysis of  $\text{NH}_3$  in Presence of  $\text{C}_2\text{D}_4$ 

$\lambda$ (Å)	Pressure (Torr)	% $\text{C}_2\text{D}_4$	Rel. Quant. $\text{H}_2$	Yield <sup>a</sup> $\text{N}_2$	% molec <sup>b</sup> $\text{H}_2$	% $\text{N}_2^b$ in Presence of $\text{C}_2\text{D}_4$	$\text{H}_2/\text{N}_2$
1849	23	13	0.19	0.09	---	---	2.1
1849	23.5	15	0.12	0.06	---	---	2.0
1849	20	0	4.96	1.54	---	---	3.2
1849	20	0	2.21	1.12	---	---	2.0
	23.5	15	0.13	0.07	5.9	6.3	1.9
1849	20	0	1.94	0.45	---	---	4.3
	23.5	15	0.05	0.02	2.6	4.4	2.5
1470	23	13	0.18	0.10	---	---	1.8
1470	23	13	0.15	0.09	---	---	1.7
1470	20	0	3.74	0.93	---	---	4.0
	21	5	0.69	0.57	18	61	1.2
1470	20	0	3.01	0.63	---	---	4.8
	23	13	0.47	0.26	16	33	1.8
1236	21	5	9.16	3.86	---	---	2.4
1236	20	0	20.2	3.76	---	---	5.4
	23	13	3.29	1.21	16	32	2.7
1236	20	0	8.16	2.34	---	---	3.5
	23.5	15	1.00	0.43	12	18	2.3
1236	8	25	0.36	0.16	---	---	2.3
1236	24	25	0.39	0.18	---	---	2.0

(a) defined as  $\frac{\text{Pressure (millitorr) of product in reaction volume}}{\text{Fraction of radiation absorbed by } \text{NH}_3 \times \text{photolysis time}}$

(b)  $\frac{\text{H}_2 \text{ (or N}_2\text{) formed in presence of C}_2\text{D}_4}{\text{H}_2 \text{ (or N}_2\text{) formed in absence of C}_2\text{D}_4} \times 100$

of 3.5<sup>5</sup> and 2%<sup>6</sup> previously reported using C<sub>2</sub>D<sub>4</sub> and value less than 5%<sup>7</sup> using O<sub>2</sub> as a scavenger for H atoms. It is therefore concluded that the principal primary process in this region is



The demonstration in the present experiments that the N<sub>2</sub> yield in photolysis of NH<sub>3</sub> + C<sub>2</sub>D<sub>4</sub> is also reduced to an average of about 5% of its value in absence of C<sub>2</sub>D<sub>4</sub> is consistent with the mechanism summarized in reactions (0) through (4). The most important conclusion from the present series of experiments is that in the presence of C<sub>2</sub>D<sub>4</sub>, reactions involving NH<sub>2</sub> radicals do not lead to production of N<sub>2</sub>. Whether this is due to suppression of the sequence of reactions (1), (2), and (4) or to suppression of reaction (8) cannot be determined at present. If all of H atoms are scavenged by C<sub>2</sub>D<sub>4</sub>, the residual small amount of H<sub>2</sub> and N<sub>2</sub> may be produced by reaction (8) since the ratio of H<sub>2</sub> to N<sub>2</sub> is approximately two in the presence of C<sub>2</sub>D<sub>4</sub>.

1.2.2 Photolysis at 1470 Å: The results in table 1 show that the hydrogen yield in the presence of 5 or 13% C<sub>2</sub>D<sub>4</sub> is reduced to an average of 17% of that observed in the absence of C<sub>2</sub>D<sub>4</sub>. A value of 12%<sup>6</sup> has been obtained previously by the same method. In contrast to the results obtained at 1849 Å however, the nitrogen yield in the presence of C<sub>2</sub>D<sub>4</sub> is substantial. Since the major difference between photolysis at the two wavelengths is the production of NH at 1470 Å, formation of N<sub>2</sub> in the presence of C<sub>2</sub>D<sub>4</sub> must result from some reaction of the NH radical.

If the exclusive fate of NH were re-combination via reaction (9), the sequence (7) plus (9) would lead to H<sub>2</sub>/N<sub>2</sub> ratio of 3. Reaction of NH with NH<sub>3</sub> in the manner suggested by Foner and Hudson<sup>12</sup>

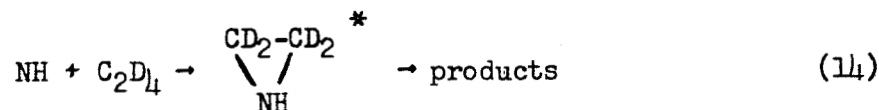


also leads to a value of  $\text{H}_2/\text{N}_2 = 3$ . Since values less than 2 have actually been observed (table 1), other reactions of NH must be sought. Two such possible reactions are



either being followed by reaction (4) to form  $\text{N}_2$ . Reaction (12) may be particularly favored since removal of H atoms via this reaction with  $\text{C}_2\text{D}_4$  should lead to a higher concentration of  $\text{N}_2\text{H}_4$  as a result of the suppression of reaction (2). The occurrence of the sequence of reactions (7), (12) or (13), and (4) should result in a minimum value of 2 for the ratio  $\text{H}_2/\text{N}_2$  if all NH radicals react with  $\text{N}_2\text{H}_4$  or  $\text{NH}_2$ .

Contribution from the reaction of NH with  $\text{C}_2\text{D}_4$ <sup>13</sup>



should lead to higher ratios of  $\text{H}_2/\text{N}_2$ . While the observed trend to higher values of  $\text{H}_2/\text{N}_2$  with increasing  $\text{C}_2\text{D}_4$  (table 1) is qualitatively consistent with the occurrence of reaction (14) in addition to (12) or (13), the actual values of the ratios (1.2 with 5%  $\text{C}_2\text{D}_4$  and 1.8 with 15%  $\text{C}_2\text{D}_4$ ) are lower than required by the mechanism. A systematic error in measuring the ratio of  $\text{H}_2$  to  $\text{N}_2$  by mass spectrometry could be responsible, although considerable attention was paid to the problem of the conditions governing relative sensitivities of  $\text{H}_2$  and  $\text{N}_2$  in the mass spectrometer. The fact that hydrogen yields in presence of  $\text{C}_2\text{D}_4$  are consistent with those obtained by previous investigators<sup>6</sup> leads us to believe that no systematic error in  $\text{H}_2\text{-N}_2$  analysis has been made.

The conclusions drawn from the experiment at 1470 Å are therefore that NH radicals react mainly with N<sub>2</sub>H<sub>4</sub>, NH<sub>2</sub>, and to a considerably less extent with C<sub>2</sub>D<sub>4</sub>. Recombination to N<sub>2</sub> + H<sub>2</sub> (reaction 9) seems to be unimportant. Therefore, the identification of the amount of hydrogen formed in presence of C<sub>2</sub>D<sub>4</sub> with the relative importance of the primary event

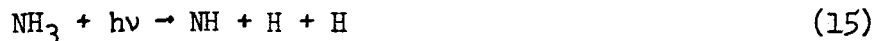


seems justified and no downward revision of the importance of (7) is required.

1.2.3 Photolysis at 1236 Å: The results in table 1 show that the hydrogen yield in the presence of ~14% C<sub>2</sub>D<sub>4</sub> is reduced to an average of 14% of that observed in the absence of C<sub>2</sub>D<sub>4</sub>. This is same average value obtained by McNesby, Tanaka and Okabe<sup>5</sup> for 5 to 25% C<sub>2</sub>D<sub>4</sub> and indicates that complete scavenging of H atom was attained in these experiments.

As in photolysis at 1470 Å, N<sub>2</sub> production in the presence of C<sub>2</sub>D<sub>4</sub> is again substantial. However, the ratio H<sub>2</sub>/N<sub>2</sub> is greater than 2 at 1236 Å. This suggests that in addition to reactions (12) and (13) which lead to a maximum value of H<sub>2</sub>/N<sub>2</sub> 2, reactions of NH leading to ratio of H<sub>2</sub>/N<sub>2</sub> > 2 must be occurring. Contribution from either NH recombination [reaction (9)] or reaction with NH<sub>3</sub> [reactions (10) and (11)] would be consistent with this result since they lead to a H<sub>2</sub>/N<sub>2</sub> ratio of 3. While there is no apparent reason why reaction between NH and NH<sub>3</sub> should occur in photolysis at 1236 Å but not at 1470 Å, NH recombination would be enhanced if the steady state concentration of NH were considerably higher at the shorter wavelength. Since both absorbed

intensities and the relative importance of reaction (7) are comparable at 1470 Å and 1236 Å, the increase in NH concentration probably results from the occurrence of the additional primary process



which is energetically possible at 1236 Å but not at 1470 Å. Our results are at least not inconsistent with the occurrence of (15) at 1236 Å. This interpretation requires that the H atom concentration in the photolysis of pure NH<sub>3</sub> be higher at 1236 Å than at 1470 Å. This has actually been demonstrated recently by Goth and Rommel.<sup>14</sup>

We therefore conclude that at 1236 Å there is some contribution to both N<sub>2</sub> and H<sub>2</sub> production from recombination of NH radicals. Thus the yield of H<sub>2</sub> from the photolysis of NH<sub>3</sub> in the presence of C<sub>2</sub>D<sub>4</sub> cannot be taken as a direct measure of the importance of



but must be corrected for contribution from



While the exact amount of this correction cannot be evaluated at present, the correction could be substantial depending on extent to which NH is formed by reaction (15) and depending on relative importance of NH recombination to reaction of NH with NH<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, or C<sub>2</sub>D<sub>4</sub>.

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## 2. SHOCK TUBE STUDIES: COLLISIONAL ENERGY TRANSFER IN FREE RADICALS

### 2.1 Introduction

Collisional processes occurring in comets can be interpreted once the vibrational relaxation and electronic transitions of the  $C_2$  and NH radical have been determined. Accordingly the present shock tube studies have been directed toward (1) the determination of the vibrational relaxation of the  $A^3\Pi_g$  state of  $C_2$  by emission spectroscopy and (2) an investigation of the singlet-triplet collisional interchange reactions by absorption spectroscopy. These processes are represented by the reaction



The current efforts for these studies have involved further instrumentation on the shock tube and the development of  $C_2$  and NH flash lamps for the absorption studies.

The vibrational relaxation of the  $A^3\Pi_g$  state of  $C_2$  can be resolved from the emission intensity for the  $v' = 0$  and  $v' = 1$  vibrational levels, measured as a function of time after passage of the shock front. Last quarter, both the integrated spectral light emission and the time-resolved emission from these levels were measured. Closer examination of the spectrographic plate indicated that the  $C_2$  formed in the shock-heated gas was in vibrational equilibrium. Continuation of the vibrational relaxation measurements will, therefore, require the proper choice of a gas mixture that will result in an inverted population.

From further consideration, it has been concluded that the singlet-triplet studies for  $C_2$  can be carried out in conjunction with the vibrational studies through absorption measurements. Of particular importance to these experiments is the availability of intense, characteristic, and sharp-lined flash lamps for the radical of interest. These lamps can facilitate the estimation of the radical concentration without the need for high-resolution spectrographs since the wavelength resolution is built into the emitter. The  $C_2$  and NH lamps developed this quarter are similar to those developed by Dr. S. H. Bauer at Cornell University, N.Y.<sup>2</sup> A picture of the lamp is shown in Figure 2-1.

The current  $C_2$  lamp emits both the Swan and Deslandres systems, but further development will be required to produce the Phillips bands. The NH lamp emits both the singlet ( $^1\Delta$ ) and triplet ( $^3\Sigma$ ) system, but further work is necessary to increase the intensity of the singlet emission. The lamp has been constructed of Pyrex with tungsten ring electrodes and filled with 5 Torr each of n-butane and helium for the  $C_2$  lamp and with 10 Torr of  $NH_3$  for the NH lamp. The proper discharge characteristics required for the emissions were produced by discharging the lamp under the conditions of varying voltage and current. In order to produce the desired emission the inductance and resistance were placed in series with the lamp.

Several improvements in the shock tube capability have been necessitated by the absorption studies. Since the absorption studies will be favored by higher pressures and therefore higher concentrations of ground states in the absorption path, work has been performed to develop diaphragms that hold higher driver gas pressures and break



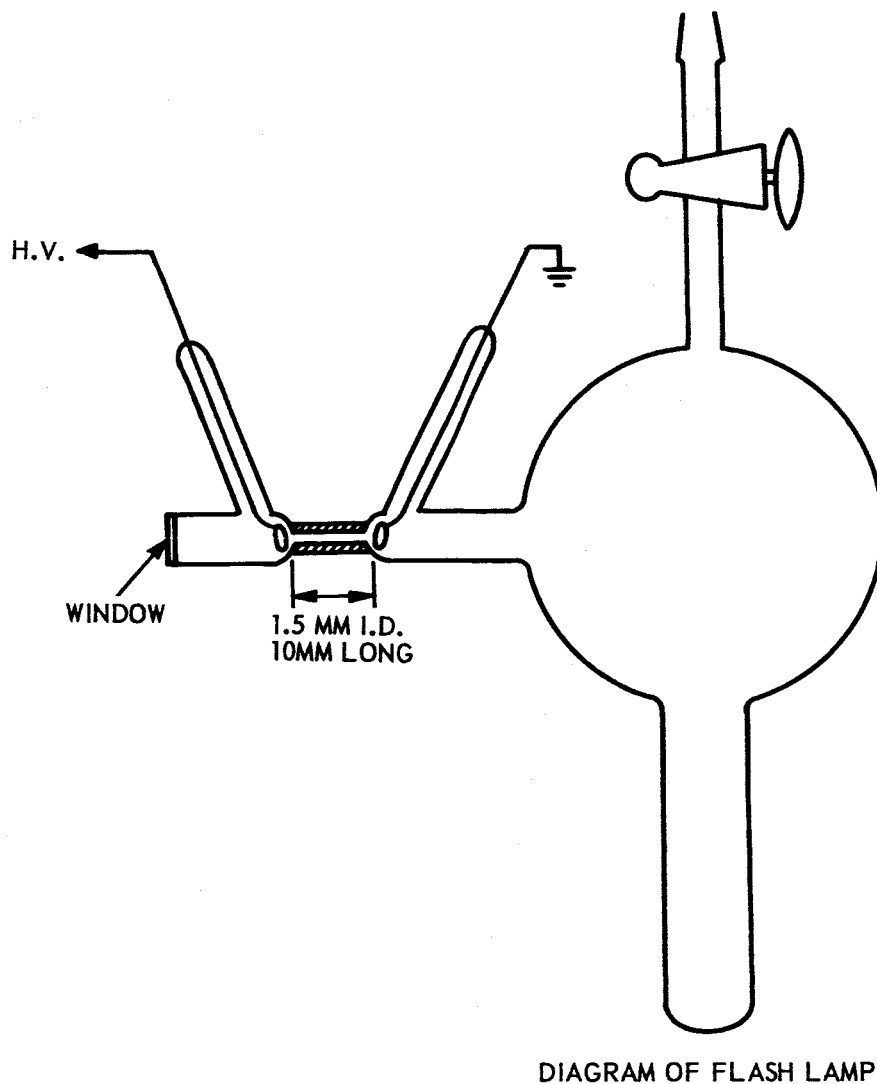


Figure 2- 1. Diagram of Flash Lamp

reproducibly. A 10-mil Mylar diaphragm scribed 5-mil deep has been found to hold 8 atmospheres of the hydrogen driver gas. For a 3000°K shock this system should allow an upstream pressure of approximately 30 Torr of argon before arrival of the shock front. This is a ten-fold improvement over the previous operational capability of this tube.

Several other improvements have been incorporated into the shock tube. New quartz windows have been mounted in the tube wall to allow absorption measurements to be made. These have been sealed in the tube with epoxy cement so that they are flush with the inside of the tube wall. The tube has been lengthened to increase the testing time at the absorption position, and newly constructed heat-transfer gauges have been placed two inches on either side of this position in order to measure the shock velocity. The gauges were constructed by painting a film of Liquid Bright Platinum on the end of a polished Pyrex rod and fired close to the softening point of the Pyrex. This process results in a more sturdy gauge than those previously used.

A diagram of the experimental arrangement and shock tube electronics is shown in Figure 2-2. The arrival of the shock front at the first heat-transfer gauge triggers the flash lamp through the circuit shown in the figure. The characteristic lines from the lamp, in this case the 3852.2 Å line corresponding to the O-O transition of the Deslandres system ( $c^1\Pi_g \rightarrow b^1\Pi_u$ ) and the 5165.2 Å line corresponding to the O-O transition of the Swan system ( $A^3\Pi_g \rightarrow X^3\Pi_u$ ), are filtered through the monochromators. The absorption of these lines as a function of time after passage of the shock front is recorded simultaneously on the chopped sweep of an oscilloscope. The signals from the two

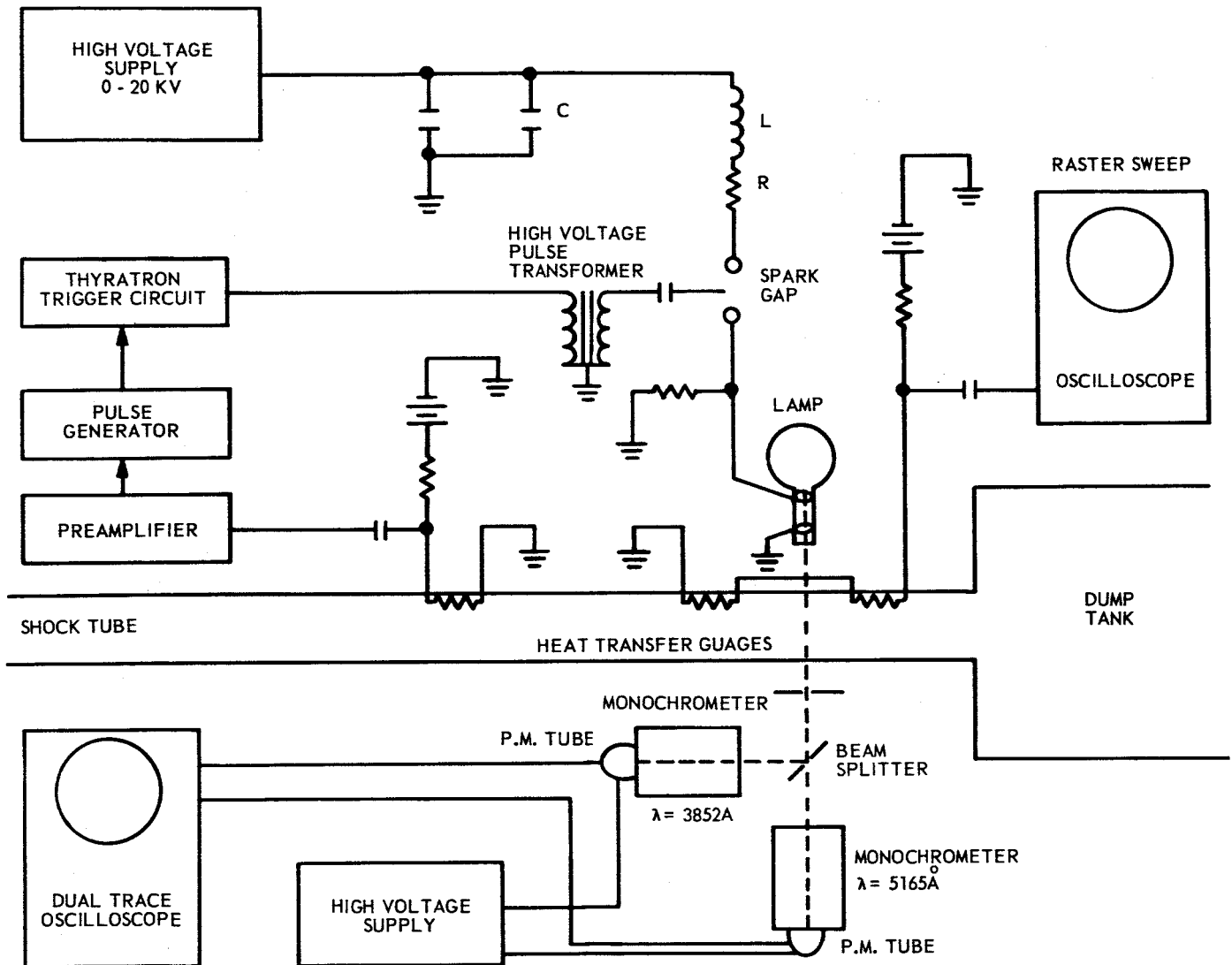
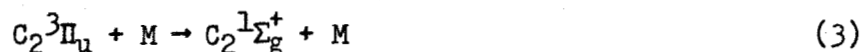


Figure 2- 2. Diagram of Experimental Arrangement and Shock Tube Electronics

heat-transfer gauges on either side of the absorption windows are displayed simultaneously on a separate oscilloscope. The temperature and pressure of the shocked gas can be determined from the shock velocity and the gas composition.

## 2.2 Results and Discussion

The spectral output of the  $C_2$  flash lamp fired at 15KV and 1.5 $\mu$ f with 150 and 300 $\mu$ H in series is shown in Figure 2-3. The triplet and singlet systems of  $C_2$  are marked in the figure along with some bands of CH and CN. The exposure was recorded with a Hilger 498 medium quartz spectrograph using 10-micron slits and 103a-F film. Twenty-five flashes resulted in the exposure shown in Figure 2-3. The time duration of the lamp under the above conditions was approximately one millisecond. The lamp output vs. time for firing under the above conditions is shown in Figure 2-4. This time can be varied by changing the amount of resistance in series with the lamp, an increase in resistance resulting in an increase in the flash duration. Preliminary observation of the spectra of the lamp in the 7000 to 9000 Å region using a Bass-Kessler grating spectrograph with 1-N plates has failed to show any Phillips band emission. Production of this system in a lamp would facilitate observation of absorption from the  $X^1\Sigma$  ground state and, therefore, measurement of the collisional interchange reaction



However, this system is much weaker than the Swan or Deslandres systems and will therefore be more difficult to observe spectroscopically.<sup>3</sup>

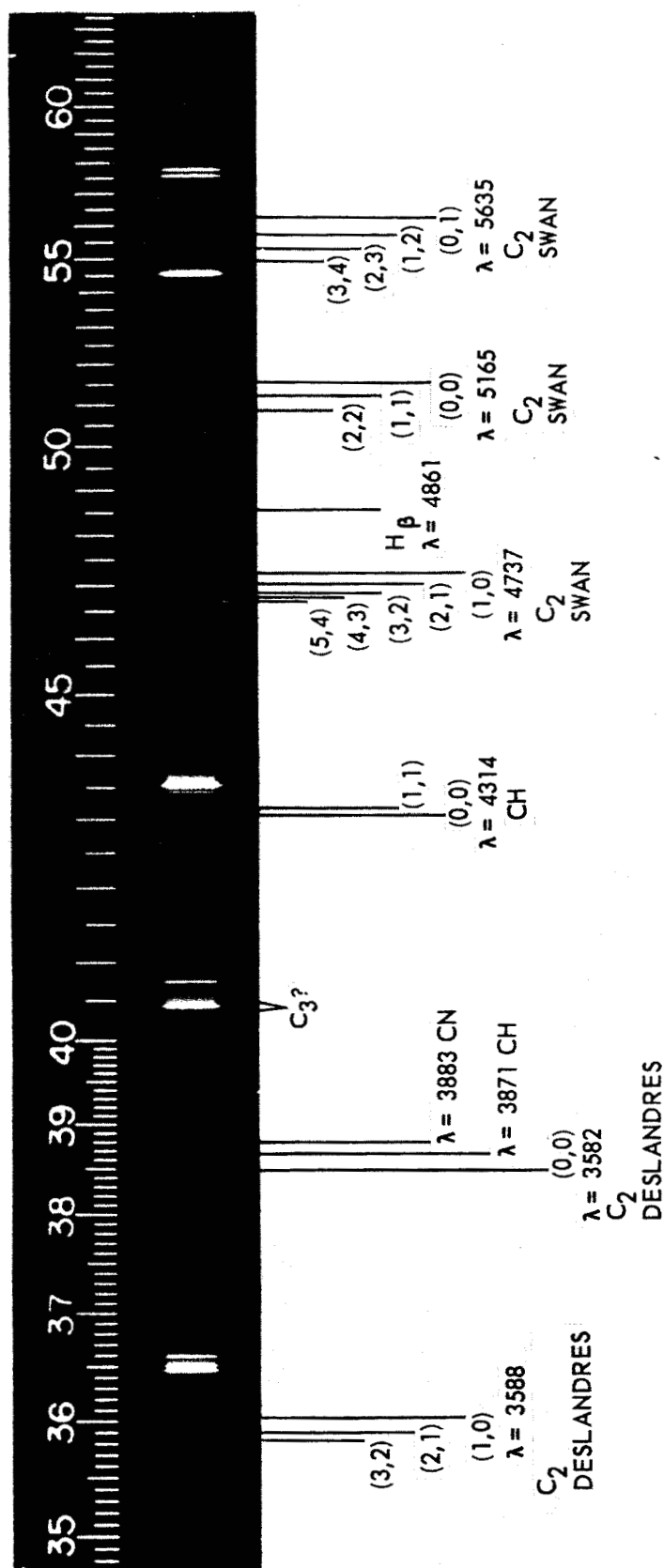


Figure 2-3. Spectrum Emitted by Flash Lamp. The Very Dark Lines on the Spectrograph are Mercury Reference Spectra

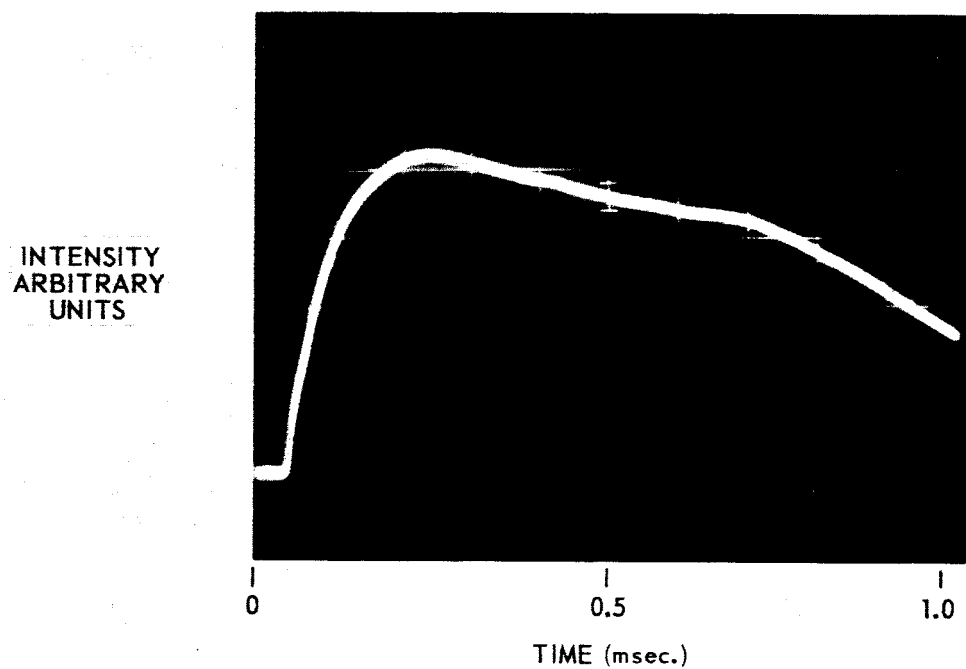


Figure 2-4. Time Variation of Flash Lamp Intensity

Better records of the emission of the lamp will be needed before the  $C_3$  emission at  $4050 \text{ \AA}$ , marked on the spectrographic record with a question mark, can be confirmed.  $C_3$  emission in the lamp would allow  $C_2 \rightarrow C_3$  reactions to be monitored also by absorption measurements.

Ethylene-argon mixtures will be used initially for these studies. The dehydrogenation reaction



will readily occur at these temperatures and the hydrogen produced will help suppress carbon formation in the tube. The  $C_2$  will subsequently be formed from the pyrolysis of acetylene.

In an attempt to produce an inverted population in the vibrational levels of  $C_2$ , a mixture of acetylene and oxygen with argon instead of pure acetylene will initially be investigated. This is a likely choice since the mechanism for the production of  $C_2$  in combustion systems is probably different than that from pyrolysis.<sup>4</sup>

The shock tube is presently designed for both the emission studies necessary to measure the vibrational relaxation rates by the method used by Roth<sup>5</sup> and for the absorption measurements necessary in the triplet-singlet collisional interchange studies of  $C_2$  and  $NH$ .

### 2.3 References

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### 3. ELECTRON BOMBARDMENT OF LOW PRESSURE GASES

Results reported during the last quarter on electron bombardment of gases have been identified through spectroscopic observations as  $\text{CO}^+$  emission. Apparently with the electron tube used in these studies all gases, except  $\text{CH}_4$ , react with the hot cathode material. Future studies should use an electron beam source external to the collision chamber.